

# Stability of the Molecular Sieve Structure in Hostile Environments

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Chemistry Division*

December 7, 1970



**NAVAL RESEARCH LABORATORY**  
**Washington, D.C.**

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## DOCUMENT CONTROL DATA - R &amp; D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

## 1. ORIGINATING ACTIVITY (Corporate author)

Naval Research Laboratory  
Washington, D. C. 20390

## 2a. REPORT SECURITY CLASSIFICATION

Unclassified

## 2b. GROUP

## 3. REPORT TITLE

STABILITY OF THE MOLECULAR SIEVE STRUCTURE IN HOSTILE ENVIRONMENTS

## 4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Final report on this phase of the problem; work is continuing on other phases

## 5. AUTHOR(S) (First name, middle initial, last name)

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## 6. REPORT DATE

December 7, 1970

## 7a. TOTAL NO. OF PAGES

11

## 7b. NO. OF REFS

12

## 8a. CONTRACT OR GRANT NO.

NRL Problem C08-05

## b. PROJECT NO.

SF 35433002-13224

## c.

## d.

## 9a. ORIGINATOR'S REPORT NUMBER(S)

NRL Report 7201

## 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

## 10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribution is unlimited.

## 11. SUPPLEMENTARY NOTES

## 12. SPONSORING MILITARY ACTIVITY

Department of the Navy (Naval Ship Systems Command), Washington, D. C. 20360

## 13. ABSTRACT

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Molecular sieves CO <sub>2</sub> absorption H <sub>2</sub> O absorption CO <sub>2</sub> capacity Regenerable systems						

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## AUTHORIZATION

NRL Problem C08-05  
Project SF 35433002-13224

Manuscript submitted September 24, 1970.

## STABILITY OF THE MOLECULAR SIEVE STRUCTURE IN HOSTILE ENVIRONMENTS

### INTRODUCTION

Several proposals have been made for systems that use molecular sieves to remove  $\text{CO}_2$  from environmental atmospheres (1-8). These materials have many favorable properties for application as regenerable  $\text{CO}_2$  removal agents in nuclear submarines. Factors of importance arising from the composition of the material are the relative chemical inertness and physical strength of these alumina-silicates. Molecular sieves, being solid before and after absorption, have no vapor pressure, a large absorption-area-to-mass ratio, and low friability and toxicity; they are also easily handled and stored. The hard, chalklike character of the crystal enables their formulation with a bonding agent which permits compaction into uniformly sized pellets or granules having good rigidity and pressure drop characteristics. The inertness of the material minimizes hazards from "dusting" or from bed destruction through contact with  $\text{H}_2\text{O}$ .

Desorption of  $\text{CO}_2$  from molecular sieves can be accomplished by several means, including thermal, evacuation, displacement by another absorbate, purging, or a combination of these methods. The only method applicable for nuclear submarine service would be the combination of heating following by evacuation. The main difficulty with this method is applying heat to the sieve. The method usually used is to place resistance heaters in or around the bed. With this type of heating, the thermal distances must be kept very short due to the poor thermal conductivity of the sieve. Short thermal distances indicate large surface areas of heaters, which, in turn, indicate bulkier beds, poor gas flows, and increased pressure drops. Also, for increased rate of heat transfer, the thermal gradient should be as large as possible, but hot spots must be avoided because the molecular sieve is only thermally stable to about  $538^\circ\text{C}$  (9).

A more efficient and rapid method of raising the temperature of a sieve bed would be to pass a hot gas through the bed. In a submarine system, the most practicable gas for this purpose would be  $\text{CO}_2$ . A system using this principle has been proposed by Musick and Smith (1). They proposed a redundant system, each unit consisting of a water-absorbing bed containing molecular sieve type 13X (sodium base - 10A pore diameter) in series with a  $\text{CO}_2$  absorbing bed containing molecular sieve type 5A (calcium base - 5A pore diameter). During the regeneration cycle, the 5A sieve would be exposed to  $\text{CO}_2$  at  $150^\circ\text{C}$  and the 13X sieve to the process air at  $300^\circ\text{C}$ . They further anticipated that the sieves, particularly the 13X, would coabsorb other contaminants known to be in submarine air. These contaminants were loosely identified as organics, and prior studies had shown that characteristic aliphatics and aromatics were readily desorbed from sieves by water displacement or by moderate heat in a moist air stream. Since the time of that report, however, a variety of halogenated hydrocarbons were finding widespread use as solvents and refrigerants in submarine systems. These materials are moderately inert and innocuous enough in themselves, but their decomposition products are reactive and corrosive. Cannon (10) has reported incipient decomposition of fluorinated methane on molecular sieves at  $25^\circ\text{C}$ , accompanied by evidence of reduced absorption capacity. For this reason it became of interest to determine the stability of the candidate sieves in these potentially hostile environments.

Dichlorodifluoromethane [R12], a common refrigerant of rather high thermal stability (11), was chosen as the test contaminant gas. Sieves of the 5A and 10A type were obtained from each of two commercial sources, and both types were subjected to all of the environments, although the proposed system would not require such exposures. The stability criterion used in all tests was the  $\text{CO}_2$  or  $\text{H}_2\text{O}$  capacity of a given sieve before and after thermal cycling in a given environment. (It must be emphasized here that a change in the capacity of a given sample is the only effect being studied and that no inter-comparison between samples as to absolute capacity is warranted or relevant.) The purpose of the study was strictly one of relative resistance to chemical degradation.

## GENERAL EXPERIMENTAL BACKGROUND

The effect of repetitive thermal cycles in  $\text{CO}_2$  and  $\text{CO}_2$ - $\text{H}_2\text{O}$  environments was studied to establish baseline capacities and to insure that any structural damage noted was the result of an R12 reaction alone.

All capacity data were obtained using a Mettler thermoanalyzer operated in the thermal gravimetric analysis (TGA) mode. In this configuration, the instrument detects and records changes in the mass of a substance being subjected to controlled thermal and/or chemical environments.

In the case of the  $\text{CO}_2$  and  $\text{CO}_2$ - $\text{H}_2\text{O}$  studies, the entire experiment was performed in this instrument. Because of the corrosive nature of the breakdown products from R12, the sieve exposures in those runs were made externally, with original and final capacity values being obtained on representative sample fractions in the thermoanalyzer.

## $\text{CO}_2$ AND $\text{CO}_2$ - $\text{H}_2\text{O}$ COMPATIBILITY

The typical procedures for each of the four samples was to place a tared sample on the sample-holder in the thermobalance and obtain equilibrium baseline weights in air and in dry  $\text{CO}_2$  at both  $25^\circ\text{C}$  and  $500^\circ\text{C}$ . The weight difference at equilibrium between air and  $\text{CO}_2$  at each of the temperatures represented the baseline  $\text{CO}_2$  capacity for that sieve. Thermal cycling between  $25^\circ$  and  $500^\circ\text{C}$  was then initiated in both dry and wet  $\text{CO}_2$  atmospheres. Periodically, the baseline  $\text{CO}_2$  absorption capacity was redetermined.

The composite results of these runs are shown in Table 1. The relatively minor variations in capacity shown are within the errors inherent to the measurements. The error sources, some of which tend to cancel, include variations in atmospheric pressure over the several days involved in a given run, variations in the sample buoyancy with differing gas densities in the balance, and lack of exact control of the  $\text{CO}_2$  partial pressure in the reference gas used for capacity checks. With these factors in mind, it can be reasonably assumed that this study has revealed no deterioration of these molecular sieves as a result of exposure to either wet or dry  $\text{CO}_2$  at temperatures up to  $500^\circ\text{C}$ .

## DICHLORODIFLUOROMETHANE [R12] COMPATIBILITY

The compatibility of R12 with both sieve types was tested in three different modes relating to environments a sieve might be exposed to in an operating system. Two modes compared the relative  $\text{CO}_2$  absorption capacity of both the 5A and 10A sieves before and after exposure to a hot, dry R12-air mixture and before and after exposure to a hot, dry R12- $\text{CO}_2$  mixture. The third mode compared the relative capacity for  $\text{H}_2\text{O}$  absorption before and after exposure to a hot, moist R12-air mixture. The first test simulated the environment if sieves containing R12 were heated in the presence of air, the second, the

Table 1  
Thermal Effect of CO<sub>2</sub> and CO<sub>2</sub>-H<sub>2</sub>O Environments on CO<sub>2</sub> Capacity

Exposure Sequence	Manufacturer X				Manufacturer Y			
	5A Sieve		10A Sieve		5A Sieve		10A Sieve	
	Wt* Change (%)	Cycles	Wt* Change (%)	Cycles	Wt* Change (%)	Cycles	Wt* Change (%)	Cycles
Start	15.2	1	15.8	1	12.8	1	18.4	1
Dry CO <sub>2</sub> , 25° C-500° C	15.2	5	15.8	6	12.8	2	18.8	9
H <sub>2</sub> O-CO <sub>2</sub> , 25° C-500° C	---	7	---	7	---	5	---	18
Dry CO <sub>2</sub> , 25° C-500° C	15.0	2	16.7	4	12.3	10	18.1	2
H <sub>2</sub> O-CO <sub>2</sub> , 25° C-500° C	---	---	---	---	---	2	---	2
Dry CO <sub>2</sub> , 25° C-500° C	---	---	---	---	12.7	19	18.1	8

\*Relative CO<sub>2</sub> capacity.

effect if the heat exchanger gas (CO<sub>2</sub>) was to become contaminated with R12, and the third, the effect of R12 in the presence of moisture and air on the capacity of the H<sub>2</sub>O absorption bed. The rating criterion in the latter test was the relative capacity for H<sub>2</sub>O absorption before and after exposure to the R12-containing gas stream. Only one sample of each type of sieve was used for these tests.

In these R12 compatibility tests, the sieves were exposed to concentrations of R12 several times greater than would normally be encountered in order to accelerate the tests. Damage to the sieve was assessed by comparing before-and-after CO<sub>2</sub> capacity values obtained in the thermobalance.

A block diagram representing the nominal system used for both the R12-air and the R12-CO<sub>2</sub> tests is shown in Fig. 1. The actual apparatus and heat source differed for reasons beyond our control. A modular test setup, used for catalyst stability studies, which included a preheater, reaction tube, sampling ports, and gas analysis equipment, was available and all runs were to have been made in this apparatus. However, following completion of the 5A-R12-air runs, a priority project claimed the services of the

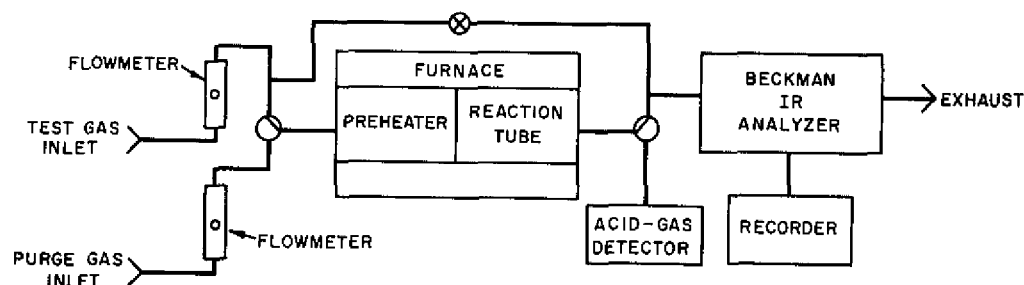


Fig. 1 - Flow diagram for CO<sub>2</sub>-R12 and R12-air exposures

apparatus, and the remaining tests were performed in an apparatus containing similar components, but without the sampling and analysis equipment.

### R12-Air Runs

The original intention was to study the decomposition rate of R12 over 5A to 10A sieves and to concurrently determine the effect on the exposed sieve. Because of the lack of analytical equipment following the 5A test, the 10A sieve was studied only under the maximum thermal regime recommended in the proposed absorber system (1).

The 5A runs were made using a dry air stream containing 5000-ppm R12 flowing through a 7/16-in.-by-7-in. reaction tube at a space velocity of 700 hr<sup>-1</sup>. The input and output gas was monitored for R12 using a Beckman infrared (ir) analyzer. Periodic analyses for acid decomposition products in the effluent were also made using the NRL strong-acid detection technique (12). As the temperature was increased, R12 decomposition was first noted at 225°C (R12 concentration in the effluent decreased). Acid gas decomposition products were also detected in the effluent. The decomposition rate increased rapidly with further increases in the temperature until essentially no undecomposed R12 was present at 315°C. After holding at this temperature for 12 hours, R12 again appeared in the effluent, the concentration rising, even when the temperature was raised to as high as 425°C, until all of the input R12 was passing through the bed unchanged. A plot of the decomposition rate of R12 versus temperature is shown in Fig. 2.

Upon removal of this test sieve from the reactor, a visual examination showed no evidence of physical damage, but the thermobalance revealed that the material had lost all capacity for CO<sub>2</sub> absorption, the sieve structure having apparently been completely destroyed by the R12 decomposition products.

The 10A-R12-air run was made in a 3/8-in.-by-3-in. stainless-steel tube heated to 300°C for 12 hours with an air stream containing about 1% R12 flowing at a space velocity of 700 hr<sup>-1</sup>. Under these conditions, this sieve lost 38% of its CO<sub>2</sub> capacity, indicating considerable structural damage.

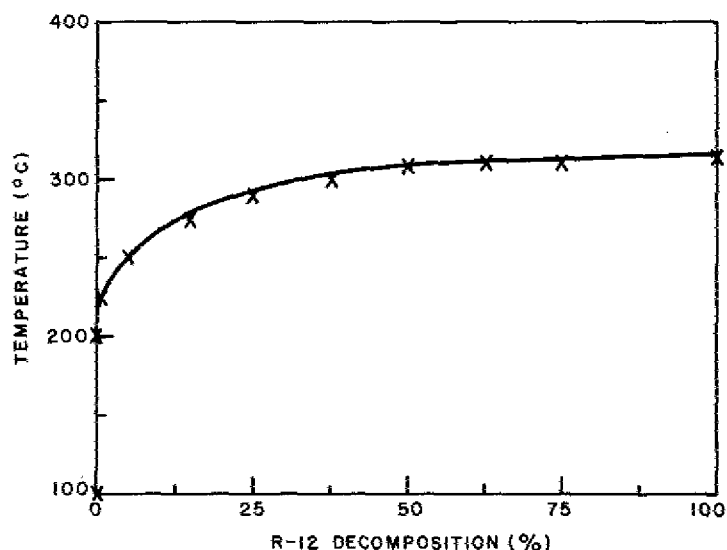


Fig. 2 - R12 decomposition rate over the 5A molecular sieve



From the decomposition rate of R12 over the 5A sieve at 300° C shown in Fig. 2, and assuming that the rate over the 10A sieve is similar, it seems certain that the 10A sieve was exposed to much less R12 decomposition products than the 5A sieve. The two sieves would probably show similar, though not necessarily equal, stability under comparable conditions.

#### R12-CO<sub>2</sub> Runs

The R12-CO<sub>2</sub> runs were made in the same apparatus and under the same flow conditions as the 10A-R12-air runs except that CO<sub>2</sub> containing about 1% R12 was the test gas, and the runs were made for extended periods of time at progressively higher temperatures until significant decomposition was indicated by the capacity checks in the thermobalance. The results for the temperatures of interest are shown in Table 2. The stabilities are in good general agreement with those for the air runs, indicating that the observed effect is a result of the R12 products alone and not a synergistic or dual reaction affected by air or CO<sub>2</sub>.

Table 2  
Thermal Effect of CO<sub>2</sub> and 1% R12 Environment on CO<sub>2</sub> Capacity

Type Sieve	Temp. of Bed and Gas (° C)	Exposure Time (hr)	Decrease in Capacity for Absorbing CO <sub>2</sub> (%)
10A	150	92	13.1
10A	250	92	53.0
5A	250	92	0.0
5A	300	160	100.0

#### R12-Air-H<sub>2</sub>O Vapor Runs

A block diagram of the experimental setup for the R12-air-H<sub>2</sub>O vapor runs is shown in Fig. 3. Air containing 1% R12 and saturated with H<sub>2</sub>O vapor at 25° C was passed through a 3/8-in. I.D. Pyrex tube that contained sieve separated into three sections by glass wool pads. Each section contained a bead of sieve treated to indicate H<sub>2</sub>O saturation. The gas mix was passed through the system at 25° C until the downstream beads indicated moisture breakthrough. The absorption cycle was stopped just as the last bead indicated H<sub>2</sub>O presence. The apparatus was then placed in a furnace at the test temperature (350° C) and back-flushed with preheated air. This treatment simulated the cyclic conditions in a H<sub>2</sub>O absorption bed wherein it was anticipated that any absorbed R12 would be desorbed before the R12 decomposition temperature was reached.

Both sieve types, after 20 cycles from 25° to 350° C, were analyzed for H<sub>2</sub>O absorption capacity in the thermobalance. The test sieves were partitioned into five fractions representing longitudinal sections down the reactor for these analyses. The results are shown in Table 3, along with the relative capacity data for unexposed sieves. The reason for the low value exhibited by section 5 of the 10A sieve experiment is not readily apparent, but it probably indicates that a higher concentration of R12 remained at this portion of the bed when the tube was placed in the furnace.

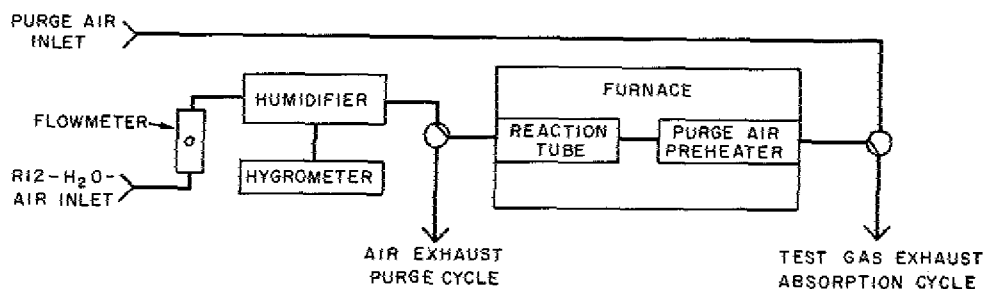
Fig. 3 - Flow diagram for R12-air-H<sub>2</sub>O vapor exposures

Table 3  
Thermal Effect of R12 Environment on H<sub>2</sub>O Capacity

Sample Fraction Number	Water Capacity (% of dry weight)	
	10A Sieve	5A Sieve
1	17.7	24.5
2	19.7	22.5
3	18.4	23.5
4	18.0	23.5
5	14.9	23.4
Average of test sieves	17.7	23.4
Unexposed sieve	27.1	25.5

## SUMMARY

Table 4 summarizes the results of the tests. It can be seen that both sieve types are quite stable, both thermally and chemically, in CO<sub>2</sub> and CO<sub>2</sub>-H<sub>2</sub>O environments to well above the contemplated regeneration temperatures, and no degradation of performance should result from exposure to these pure gases. On the other hand, the presence of halogenated compounds is shown to be deleterious at temperatures which coincide closely with those required for H<sub>2</sub>O bed regeneration. The sieve of choice (5A) for CO<sub>2</sub> absorption should be stable at the 150° C required for CO<sub>2</sub> regeneration, if no hot spots are encountered. The substitution of the 5A sieve for the 10A sieve in the H<sub>2</sub>O bed would help, but not eliminate, the potential hazard.

The experiments indicated that acid decomposition products, other than the pure halocarbon, were the reactive species, but it was also shown that molecular sieves catalyze or, at least, promote decomposition of these compounds at temperatures below those at which they are normally stable.

The presence of potentially reactive compounds as impurities in the purge gases or as retained absorbates on molecular sieves could cause a serious cumulative loss in operating efficiency as a result of reactive decomposition with accompanying sieve structure destruction at the temperature required for a regenerative system.

Table 4  
Summary of Environmental Test Results

Test Environment	Sieve Type	Relative Stability of Sieve
CO <sub>2</sub> Multicyclic exposure between 25° and 500° C	5A	No change in CO <sub>2</sub> capacity
	10A	No change in CO <sub>2</sub> capacity
CO <sub>2</sub> -H <sub>2</sub> O Multicyclic exposure between 25° and 500° C	5A	No change in CO <sub>2</sub> capacity
	10A	No change in CO <sub>2</sub> capacity
R12-air 12 hours at 315° C - 3 hours at up to 425° C - 0.5% R12 12 hours at 300° C - 1% R12	5A	100% loss of CO <sub>2</sub> capacity
	10A	38% loss of CO <sub>2</sub> capacity
R12-CO <sub>2</sub> 92 hours at 250° C - 1% R12 160 hours at 300° C - 1% R12 92 hours at 150° C - 1% R12 92 hours at 250° C - 1% R12	5A	No change in CO <sub>2</sub> capacity
	5A	100% loss of CO <sub>2</sub> capacity
	10A	13% loss of CO <sub>2</sub> capacity
	10A	53% loss of CO <sub>2</sub> capacity
R12-air-H <sub>2</sub> O Multicyclic saturation with H <sub>2</sub> O and R12 at 25° C - regeneration at 350° C - 1% R12	5A	8% loss in H <sub>2</sub> O capacity
	10A	35% loss in H <sub>2</sub> O capacity

#### REFERENCES

1. Musick, J. K., and Smith, S. H., "Molecular Sieves for Removal of Carbon Dioxide from Submarine Atmospheres," NRL Memorandum Report 874, Dec. 1958
2. Ebeling, R. W., Jr., Kratz, W. C., and Singleton, A. H., "Investigation of the Thermoelectric Adsorber Concept for Carbon Dioxide Removal from Breathing Atmospheres," Technical Report AFFDL-TR67-113, Wright-Patterson AFB, Ohio, Aug. 1967
3. Shearer, R. E., Betz, J. R., and King, J. C., "Recovery of Breathing Oxygen from Carbon Dioxide," MSA Research Corporation 63-14, Jan. 22, 1963
4. Wareham, B. A., "Carbon Dioxide Removal from Air in Submarines using Molecular Sieve Material, Part I" Report A/84(W), Admiralty Materials Laboratory, Holton Heath, Poole, Dorset, Feb. 1964
5. Fox, W. B., "Adsorption of Carbon Dioxide-Particle and Adsorber Configuration," Technical Report AFFDL-TR-66-126, Wright-Patterson AFB, Ohio, Oct. 1966

6. Ducros, H. , "Experimental Study in an Air Tight Cabin; of a System of Air Regeneration by Means of Molecular Sieves," FTD-TT-65-1788, Wright-Patterson AFB, Ohio
7. "Removal of Carbon Dioxide from Submarine Air with Solid Absorbents," for Department of the Navy Bureau of Ships by Lindberg Engineering Company, Chicago, Ill. , Phase I, Feb. 1958; Phase II, Dec. 1959
8. Willard, T. L. , "Research and Development on Closed Respiratory System Accessories, Molecular Sieves for Carbon Dioxide Adsorption," Minneapolis-Honeywell Regulator Company, Minneapolis, Minn. , Oct. 1961
9. Davidson Molecular Sieves, 6M-8-67, W. R. Grace Co. , Baltimore, Md.
10. Cannon, P. , "Absorption of Fluorinated Methanes by Linde Molecular Sieves," J. Phys. Chem. 63: 160 (1959)
11. Johnson, J. E. , and Musick, J. K. , "Studies of Halogenated Hydrocarbons, Part I - Stability of Fluorocarbons in Air over Hopcalite Catalyst or Stainless Steel," NRL Report 6546, May 26, 1967
12. Williams, D. D. , Johnson, E. T. , and Miller, R. R. , "A Method for the Determination of Strong Acid Vapors in the PPM Range," NRL Report 6332, Oct. 14, 1965